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THE EFFICIENCY OF UTILIZATION OF RADICALS PRODUCED
IN THE DECOMPOSITION OF AZO-BIS-ISOBUTYRONITRILE

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Abstract

It has been found that the primary products formed in the decomposition of azo-bis-isobutyronitrile cannot be scavenged quantitatively by either butyl mercaptan or diphenylpicrylhydrazyl. This behavior points to either a non-radical cleavage of the azo compound or to diffusion control of the recombination of primary products. Reasons for favoring the latter explanation are presented.

The decomposition of azo-bis-nitriles has been the subject of recent extensive study by Overberger and co-workers¹, by

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1. C. G. Overberger, H. Bilech, A. B. Finestone, J. Lilker and J. Herbert, J. Am. Chem. Soc., 75, 2080 (1953) and earlier papers in the series.
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Waters and co-workers² and by many others.³ All workers have

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2. F. J. L. Aparicio and W. A. Waters, J. Chem. Soc. 4667 (1952) and earlier papers in the series.
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3. For example, C. E. H. Bawn and S. F. Mellish, Trans. Faraday Soc., 47, 1216 (1953), Ziegler, Deparade and Meye, Annalen, 567, 141 (1950) and M. S. Matheson, E. E. Auer, E. B. Berilacqua and E. J. Hart, J. Am. Chem. Soc., 71, 2610 (1949).
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concluded that thermal decomposition at low temperatures produces radicals according to equation (1).



Recent observations in this laboratory⁴ concerning the

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4. G. S. Hammond, J. T. Rudesill and F. J. Modic, J. Am. Chem. Soc., 73, 3929 (1951).
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behavior of benzoyloxy radicals produced in the decomposition of benzoyl peroxide have suggested that some of the primary products interact before they can diffuse apart. Matheson⁵

5. M. S. Matheson, J. Chem. Phys., 13, 584 (1945).

made a similar suggestion on the basis of the rate of peroxide-induced styrene polymerization in solvents. Since peroxide decomposition is rendered complex by the occurrence of chain decomposition we have turned to a study of the primary process in the decomposition of azo-bis-isobutyronitrile (AIBN). One of several approaches involves a study of the reactivity of decomposition products toward reactive free radical scavengers. The comparison of the relative reactivity toward the scavenger as opposed to the normal reactions of the radicals with the results of similar competitive experiments with the same or similar radicals produced in other ways should shed considerable light on the importance of proximity effects in the disposition of the primary products.

Experimental

Azo-bis-isobutyronitrile was recrystallized twice from aqueous alcohol. The substance melted at 102°C with decomposition. Infrared spectra as well as nitrogen evolution experiments showed the absence of tetramethyl succinonitrile.

n-Butyl Mercaptan. Eastman Kodak white label material was dried over drierite and fractionated twice in nitrogen atmosphere. The concentrations of mercaptan in the mixtures

were accurately determined by the iodine method.⁶

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6. Sidney Siggia, "Quantitative Organic Analysis via Functional Groups", John Wiley and Sons, Inc., 1949, pp. 85-86.
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α, α -Diphenyl- β -Picryl Hydrazyl was prepared by the method of Goldschmidt and Renn,⁷ and was purified by recrystallizing

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7. Goldschmidt and Renn, Ber, 55, 628 (1922).
-

from chloroform (m.p. 140°C). Solutions of DPH in the various solvents used showed an absorption maximum at 5200 Å, obeying Beer's law throughout and beyond the range of concentrations used in the present work.

Solvents. Toluene, carbon tetrachloride, chlorobenzene and benzene was purified, dried and fractionated by usual methods.

Studies with n-butyl mercaptan: -8.20 gm. AIBN (0.05 mol.) was dissolved in 250 ml. of solvent containing known amounts of n-butyl mercaptan. The mixture contained in a liter flask was frozen in dry ice-acetone bath, evacuated and sealed under vacuum. The sealed flask was immersed in an oil bath maintained at 80 ± 0.1°C. Reaction was allowed to take place for about 20 hours which equals 16 half life periods for the decomposition of AIBN at 80°C. The flask was cooled, opened and the solvent and mercaptan evaporated off under reduced pressure at room temperature. The residue, usually a mixture of yellowish oil and white crystals, was carefully filtered, washed with cold aqueous alcohol and the solid recovered mixed with the first crop. The whole lot was then recrystallized from aqueous alcohol,

filtered, dried and weighed. The product dinitrile, melted at 167-8°C. Two control experiments in each of the two solvents, carbon tetrachloride and toluene, in absence of mercaptan gave identical yield of tetramethylsuccinonitrile (86.8 mole p.c. in toluene and 96.2 mole p.c. in carbon tetrachloride). Various experiments were run under comparable conditions to establish that neither the solvent nor the dinitrile formed are involved in any reaction with the mercaptan.

Studies with DPH. --(A) Calculated volumes of DPH and AIBN solutions were pipetted into the reaction vessel which was provided with a nitrogen bubbling device, a standard taper joint for withdrawing samples and a condenser. This was diluted with a known volume of the solvent to bring the optical density of the resultant solution to a conveniently and accurately measurable value. The concentration of AIBN used in all these experiments has been at least ten times greater than the concentration of DPH. Nitrogen gas was bubbled through the solution for a period of about ten minutes to remove the dissolved oxygen from the solution. Reaction was then started by immersing the reaction vessel in an oil bath maintained at the desired temperature, viz. 60° or 62.5°C. Throughout the whole experiment the system was kept under a slight positive pressure of nitrogen. Samples were pipetted out at different intervals into glass-stoppered 10 ml. flasks cooled in an ice bath. Optical density of the different samples were measured in a Model DU Beckman spectrophotometer. The time for complete reaction (T_1) was

determined by the method of Bawn and Mellish³. The rate of decomposition of the initiator was calculated on the assumptions that the initiator decomposes to yield two reactive free radicals each of which is terminated by one molecule of diphenyl picryl hydrazyl. In the solvents studied and within the range of concentrations employed, the results are quite reproducible.

(B) In order to exclude traces of oxygen, some sealed tube experiments were carried out in benzene solution. The reaction mixture, as before, was saturated with nitrogen, 8 ml. portions of this solution were pipetted into scrupulously cleaned test-tubes. The contents were frozen, evacuated and flushed with nitrogen and allowed to melt. The process of freezing, evacuation and flushing with nitrogen was repeated three times and the tubes were finally sealed under benzene vapor at a reduced pressure. After taking over the samples at different times during reaction at 62.5°C, the ampoules were broken open and the optical density determined.

It was not possible to detect any increase in the optical density of the samples removed from the sealed tubes after they had been exposed to the air for several hours.

Table I

Solvent; Toluene; (AIEN) = 0.20 m/l, Temp. 80°C	
Initial mercaptan concn. (m/l) x 10 ²	Yield of Dinitrile mole per cent
0.00	86.8
3.27	58.5
7.76	41.9
15.21	16.9
30.93	10.3
63.20	4.6

TABLE II

Solvent: Carbon tetrachloride, AIBN = 0.20 m/l, Temp. 80°C.

Initial mercaptan concn. (m/l) x 10 ²	Yield of Dinitrile mole per cent
0.00	96.2
9.048	41.2
17.884	18.4
36.096	18.3
53.360	15.5

TABLE III

Solvent: Carbon tetrachloride, Initiator: AIBN, Inhibitor: DPH

Run	Temp.	(DPH) x 10 ³ (m/l)	(AIBN) x 10 ² (m/l)	t _c (min)	k ₁ x 10 ⁶ Sec ⁻¹
43	60°	0.278	2.64	27	3.25
44		.278	3.961	18.5	3.17
45		.511	3.961	29	3.71
46		.128	1.321	22	3.67
51		.128	1.309	25	3.32
54		.0639	0.693	22	3.49
55		.0639	.346	42.6	3.61
56		.0639	.693	21.3	3.61
57		.0639	.519	29.5	3.47
62	62.5°	.630	4.854	- -	10.54 (a)
100		.124	.656	34	4.60
102		.0773	.492	31.5	4.16
101		.124	.656	51.	3.08 (b)
103		.0773	.492	43.5	3.09 (b)
81B	74.4°	- -	5.23	- -	11.80 (a)
105		.155	.329	25	15.71 (b)

TABLE IV

Solvent: Chlorobenzene, Initiator: AIBN, Inhibitor: DPH

Run	Temp.	$[DPH] \times 10^3$ (m/l)	$[AIBN] \times 10^2$ (m/l)	t_c (min)	$k_1 \times 10^6$ Sec ⁻¹
68	60°	0.143	0.649	27	6.82
69		.0717	.325	26	7.08
70		.0717	.195	40.5	7.57
71		.0717	.455	19.25	6.83
75		.0717	.389	21	7.30
76		.0717	.259	23.5	9.79
96		.133	.615	27.5	6.56 (b)
71B	74.4°	- -	15.2	- -	15.4 (a)
104		.120	.240	17	26.5 (b)
83B		- -	15.2	- -	78.0 (a)

TABLE V

Solvent: Benzene, Initiator: AIBN, Inhibitor: DPH

Run	Temp.	$[DPH] \times 10^3$ (m/l)	$[AIBN] \times 10^2$ (m/l)	t_c (min)	$k_1 \times 10^6$ Sec ⁻¹
78	62.5°	0.112	0.312	21	14.25
79		.112	.325	21	13.97
85		.112	.127	51	14.38
89		.112	.190	35	14.02
90		.112	.190	67	7.32 (b)
92		.112	.190	67	7.32 (b)
111		.127	.340	45.5	6.85 (b)
106B	54.3°	- -	25.0	- -	14.2 (a)
109		.127	1.58	33	2.03 (b)
110		.127	.136	26	29.98 (b)

(a) Nitrogen evolution experiment.

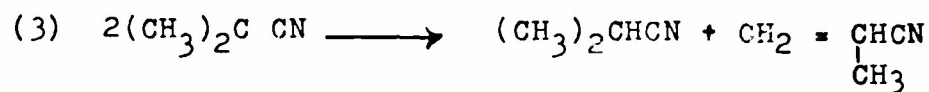
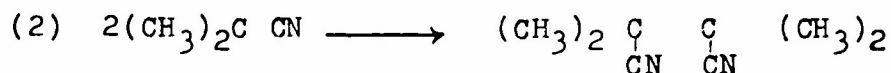
(b) Sealed tube experiment.

Results and Discussion

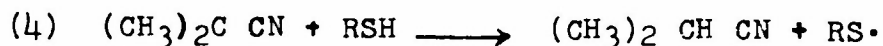
In pure toluene at 80° the decomposition of AIBN yields 86 per cent tetramethylsuccinonitrile. The work of Bickel and Waters⁸ shows that a nearly quantitative material balance can

8. A. F. Bickel and W. A. Waters, Rec. Trav. Chim., 69, 312 (1950).

be obtained in this solvent if disproportionation products as well as dimer are estimated. Therefore, no attack on the solvent occurs and reactions (2) and (3) may represent the exclusive reaction path.



If butyl mercaptan is added to the solution the yield of dinitrile is decreased, as would be expected, by the incursion of reaction (4).



Thiyl radicals produced in this manner capture some initiator fragments as has been shown by Bruin, Bickel and Kooyman.⁹

9. P. Bruin, A. F. Bickel and E. C. Kooyman, Rec. Trav. Chim., 71, 1115 (1952).

If equation (2) represented the only way in which dinitrile could be produced it would be expected that the yield would be reduced to a vanishingly small value at sufficiently high

mercaptan concentrations. That this is not the case is demonstrated by the data shown in Tables I and II. It is furthermore significant that the limiting yield of dinitrile is higher in carbon tetrachloride than it is in toluene. In the former solvent the limiting value is 15 per cent and in the latter it is 7 per cent. This seems to indicate that there is some precursor of the dinitrile which cannot be scavenged by the mercaptan.

Similar conclusions are indicated by the rates of disappearance of diphenylpicrylhydrazyl in the presence of decomposing AIBN. Bawn and Mellish³ have proposed that such experiments offer a convenient method of determining the rate of decomposition of materials which decompose at measureable rates at low temperatures. However, it is interesting to note that the reported rate of decomposition of AIBN in carbon tetrachloride is considerably slower than that expected on the basis of extrapolation of the rates at higher temperatures as determined by nitrogen evolution. Tables III-V summarize the apparent rates determined by Bawn's method and those determined at the same temperatures by nitrogen evolution. The discrepancies are general and of an important order of magnitude. In carbon tetrachloride the DPH rate is 33 per cent of the nitrogen rate. This is observed despite the fact that the rate of disappearance of DPH is zero order with respect to DPH concentration except at very low concentrations. Furthermore, the values for the extrapolated zero order lifetime of DPH are independent of the concentrations of both the initiator and the

scavenger. It is, however, disquieting to note that in chlorobenzene and benzene the lifetime was decreased appreciably by careful degassing of the solutions prior to heating. This observation was made after an attempted correlation of these results with those obtained another method of estimating efficiencies estimated by the DPH method were compared with those observed in the study of the inhibition of air oxidation in the same solvents.¹⁰ Values obtained with inhibitors in benzene

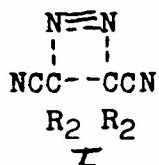
10. C. E. Boozer, G. S. Hammond and J. N. Sen, unpublished results.

solution were much lower than the DPH values. It is apparent that in the presence of traces of oxygen DPH can react with more than one chain per molecule on the average. It was at first thought that this might be due to the oxidation of diphenylpicrylhydrazine, formed by radical disproportionation, by oxygen. However, the solutions which were degassed and heated in vacuo did not regenerate the color of DPH when exposed to the air.

Unfortunately it is not convenient to carry out a direct comparison of the work with butyl mercaptan with the DPH studies. It is necessary to work at high conversions in the mercaptan experiments since the reaction product is determined. To carry decompositions to suitably high conversion at lower temperatures would become exceedingly tedious. On the other hand, at 80° the products from DPH are unstable and react further with initiator fragments.

There are two general types of explanation for these observations. The first assumes that some of the azo-nitrile decomposes to give products directly by a non-adiabatic process. The second involves the assumption that all molecules decompose to give radicals but that the rate of reaction of the primary products with each other is sufficiently rapid to become diffusion controlled to the extent that some pairs never become separated. The further assumption must then be made that the reactions with suitable scavengers are only rapid enough to be competitive for separated radicals.

The second explanation is currently held to be the more plausible. In order to adopt the first it seems inevitable that one would have to assume that the non-adiabatic decomposition involves a transition state such as I. Aside from any



discussion of the activation energy which might be involved in the formation of such a configuration it is highly probable that isomerization of the trans azo compound¹¹ to the cis

11. We believe that the arguments advanced by Overberger et al.¹¹ to the effect that only trans azo nitriles are normally encountered are convincing enough to warrant tentative acceptance.

12. C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, J. Am. Chem. Soc., 71, 2661 (1949).

would precede the actual decomposition. It would also be

required that no cis compound can accumulate in solution but rather that it must be decomposed at an immeasurably rapid rate. Otherwise disturbance of the first order rates of nitrogen evolution would be observed. The known stability of at least one cis azo compound, azobenzene, toward decomposition makes the entire picture seem doubtful. Furthermore, since the efficiencies vary much more than the decomposition rates as solvents are varied it would be necessary to assume that changes in the adiabatic rate must always be nearly compensated by changes in the non-adiabatic rate.

Such compensation would be regarded as coincidental and one feels a reluctance to accept theories which depend upon repeated coincidences.

On the other hand, the "cage effect" is merely the microscopic reverse of diffusion control of the rates of radical recombination. That such diffusion control can occur is now rather widely accepted. For example, the decrease in the rate of termination of polymer chains at high conversion has been attributed to just such behavior.¹³

13. M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *ibid.*, 71, 497 (1949).

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